

A first 1,2,4-triazole Pb^{II} Complex: Thermal, spectroscopic and structural studies, [Pb₂(trz)₂(CH₃COO)(NO₂)_n]

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Received 9 July 2006; accepted 1 August 2006

Available online 14 August 2006

Abstract

A 3D Pb^{II} coordination polymer containing 1,2,4-triazole (trz) and two different anions, [Pb₂(trz)₂(CH₃COO)(NO₂)_n], has been synthesized and characterized by elemental analysis, IR-, ¹H NMR-, ¹³C NMR spectroscopy and studied by thermal as well as X-ray crystallography. The single-crystal X-ray data shows two types of Pb²⁺-ions with coordination numbers of seven, Pb(1) and Pb(2) with *hemidirected* and *holodirected* geometries, respectively.

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Keywords: 1,2,4-triazole; PbII; Coordination polymer; Thermal properties; Lone pair

Divalent lead, with its electronic configuration [Xe]4f¹⁴5d¹⁰ 6s², is one of the post-transition metal elements that exhibits the so-called “inert-pair effect” and their compounds are interesting and frequently discussed in considering the “stereo-chemical activity” of valence shell electron lone pairs [1–5]. The lead(II) complexes with N-donor ligands [6–19] have been studied in some detail. However, a lead(II) complex involving of 1,2,4-triazole (trz) ligand have not been reported in the literature. We report here on the preparation, characterization, thermal and crystal structure of the first mixed-anion lead(II) complex involving the 1,2,4-triazole (trz) ligand.

1,2,4-triazoles have attracted great and growing interest in the coordination chemistry because of the fact that they can synthesize transition metal coordination polymers with the two bridging close adjacent nitrogen atoms (N1 and N2) or 4-positioned one (N4) and 1,2,4-triazoles also exhibiting excellent bioactivities show particular interest

for their multifarious uses in agriculture, medicine and industry [20,21].

The 1,2,4-triazole ligand because of its ability for forming polynuclear compounds may also be a very good candidate for the investigation of the “stereo-chemical activity” of valence shell electron lone pairs in the lead(II) compounds.

The title complex was prepared by the branch tube method [22]. IR spectra display characteristic absorption bands for “trz”, nitrite and acetate anions. The relatively weak absorption bands around 2920 and 3050 cm⁻¹ is due to the C–H modes involving the –CH₃ and aromatic ring hydrogen atoms, respectively. The absorption bands with variable intensity in the frequency range 1400–1590 cm⁻¹ correspond to ring vibrations of the “trz” ligand. The characteristic bands of the carboxylate group in this compound appear about 1515 *v*_{as(C–O)} and 1400 *v*_{sym(C–O)} cm⁻¹. The $\Delta\nu$ value (*v*_{as}–*v*_{sym}) is 115 cm⁻¹, indicates that the carboxylate group is coordinating with Pb in a bidentate and bridging fashion [23–25], which is unambiguously confirmed by the crystal structure of complex. The characteristic bands of the nitrite groups appear at 1134 and 1474 cm⁻¹. The ¹H NMR spectra of the DMSO

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solution of the complex displays one singlet at *ca.* 78.20 ppm assigned to the aromatic rings protons of “trz” ligand. In this compound a other signal at 1.75 ppm assigned to methyl protons of acetate anions. The ^{13}C NMR spectrum of the DMSO solution of the complex displays one distinct signal at 147.8 ppm assigned to the aromatic rings carbons of “trz” ligand. Two other signals at 26.3 ($^{13}\text{CH}_3\text{-COO}$) and 177.8 ppm ($\text{CH}_3\text{-}^{13}\text{COO}$) assigned to carbons of acetate anions.

In order to examine the thermal stability of the compound, thermal gravimetric (TG) and differential thermal analyses (DTA) were carried out for $[\text{Pb}_2(\text{trz})_2(\text{CH}_3\text{COO})(\text{NO}_2)]_n$ between 30 to 700 °C (Fig. 1). Compound does not melt and is stable up to 230 °C. The TG curve of $[\text{Pb}_2(\text{trz})_2(\text{CH}_3\text{COO})(\text{NO}_2)]_n$ indicates the release of trz molecule takes place in 230 °C with one exothermic effect at 245 °C (observed 20.10%, calcd. 20.75%) to give the product of trz-free $[\text{Pb}(\text{CH}_3\text{COO})(\text{NO}_2)]_n$, and decomposition of the acetate and nitrite anions takes place at 310 °C and the experimental mass loss of 13.35% is consistent with the calculated value 13.58% for the elimination of $\text{C}_2\text{H}_3\text{NO}_3$ of one acetate and one nitrite anion with two exothermic effects at 350 and 398 °C. The solid residue formed at around 400 °C is suggested to be PbO (observed 66.55, calcd: 65.67%).

Determination of the structure of the $[\text{Pb}_2(\text{trz})_2(\text{CH}_3\text{COO})(\text{NO}_2)]_n$ by X-ray crystallography [26] showed the complex in the solid state to be a three-dimensional coordination polymer (Fig. 2). In the structure of $[\text{Pb}_2(\text{trz})_2(\text{CH}_3\text{COO})(\text{NO}_2)]_n$, there are two different Pb atoms with coordination number of seven, PbO_4N_3 . Each lead atom is linked by three nitrogen atoms of “trz” ligands and also four oxygen atoms of nitrite and acetate anions. The “trz” anion acts as a three donor ligand and connects to three different Pb^{2+} ions (Scheme 1a and Fig. 3). The acetate and nitrite anions in this compound are coordinated as same and act as both bidentate chelating and bridging group where two oxygen atoms coordinate to a lead(II) ion, also these oxygen atoms bridge to two other lead(II) (Scheme 1b and c), resulting acetate and nitrite anions act as a four donor ligand, connecting three Pb^{2+} ions.

The arrangement of nitrogen and oxygen donor atoms around of Pb1 atom suggests a gap in coordination geometry (Fig. 4a), occupied possibly by a stereo-active lone pair of electrons on lead(II). Hence, the geometry of the nearest

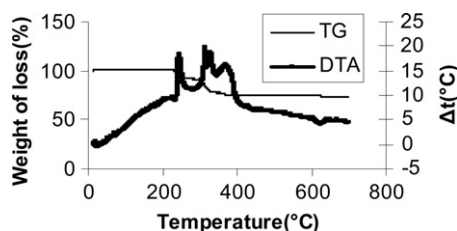


Fig. 1. Thermal behaviour of $[\text{Pb}_2(\text{trz})_2(\text{CH}_3\text{COO})(\text{NO}_2)]_n$.

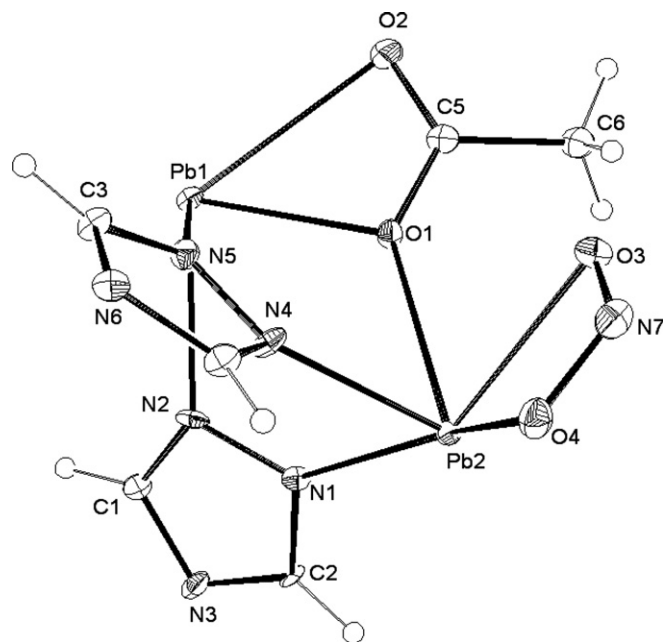
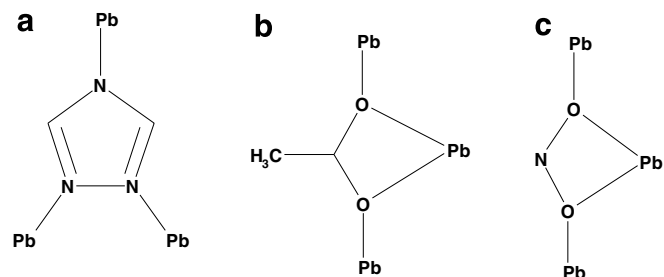


Fig. 2. X-Ray crystal structure (ORTEP representation) of $[\text{Pb}_2(\text{trz})_2(\text{CH}_3\text{COO})(\text{NO}_2)]_n$. Ellipsoids 30% probability.



Scheme 1. Schematic representation of coordination modes of “trz”, acetate and nitrite anions in the $[\text{Pb}_2(\text{trz})_2(\text{CH}_3\text{COO})(\text{NO}_2)]_n$.

coordination environment of every Pb1 atom is likely caused by the geometrical constraints of coordinated “trz”, acetate and nitrite anions and by the influence of a stereo-chemically active lone pair of electrons. Such an environment leaves space for bonding of oxygen atoms of nitrite anion of adjacent molecule with distances of $\text{Pb1-O4}^{\text{ii}} = 3.040 \text{ \AA}$ (Fig. 4a). These Pb–O distances are in the range commonly observed in the Pb-NO_2 complexes [27] and the Pb–O contacts between the metal ion and nitrite oxygen atoms observed in the title compound can definitely be considered bonding interactions. Hence, the Pb1 coordination sphere is completed and the coordination number for it to be seven (PbN_3O_4) with *holodirected* geometry [5]. In $[\text{Pb}_2(\text{trz})_2(\text{CH}_3\text{COO})(\text{NO}_2)]_n$, the arrangement of nitrogen and oxygen donor atoms around of Pb2 atom does not suggest a gap in coordination geometry (Fig. 4b) and the lone pairs of Pb2 is ‘inactive’ in the solid state. Hence, whereas the geometries with respect to Pb1 may be considered as *holodirected*, that regarding Pb2 is surely *holodirected*. The *holodirected* geometry with seven

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